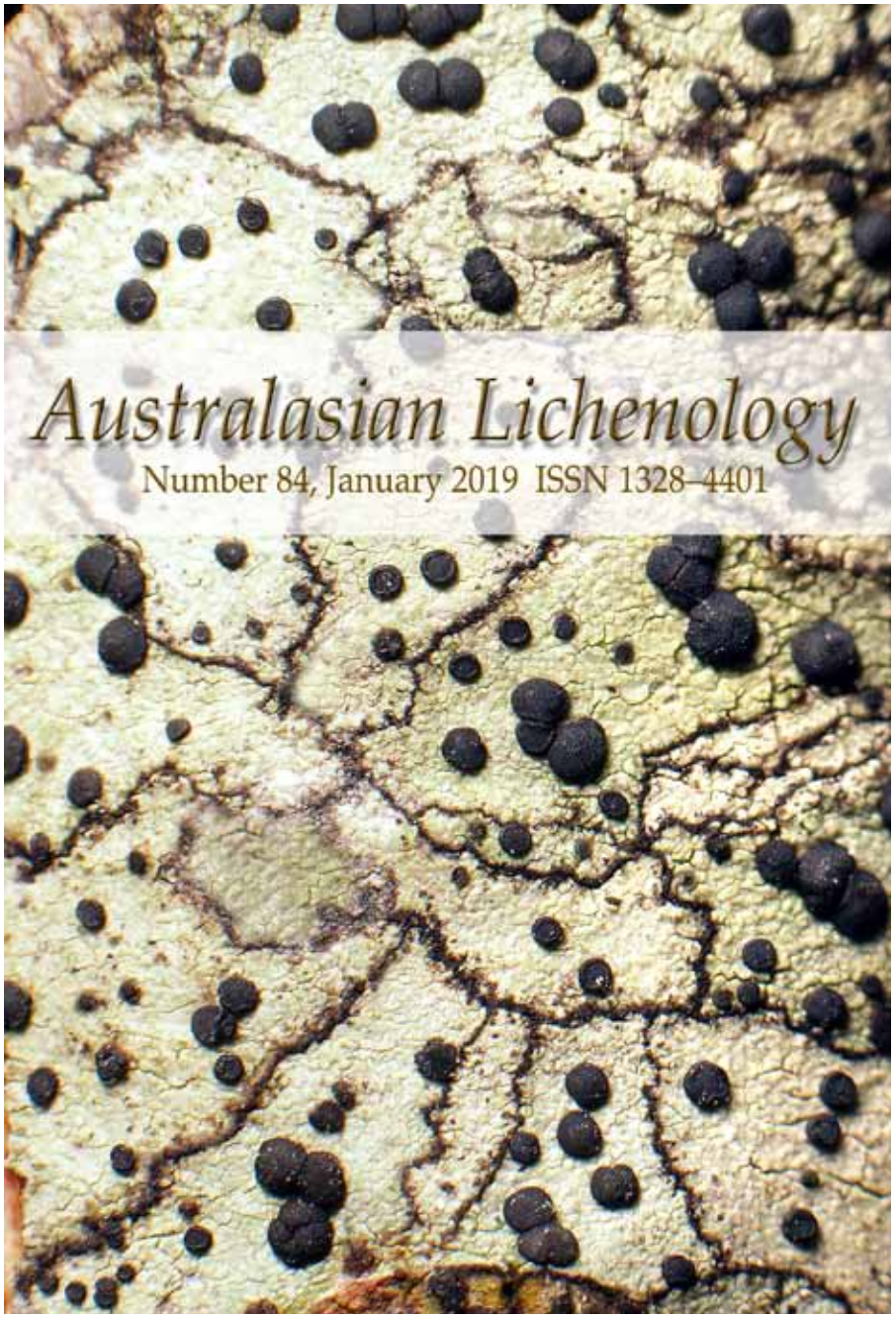

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The cosmopolitan *Lecidella elaeochroma* is common on smooth-barked trees and shrubs in forests and cityscapes throughout Australia and New Zealand (also throughout Europe, the Americas, Macaronesia, Asia and Africa). Its dark marginal prothalli can form complex mosaics. Its chemistry is largely xanthones, among them arthothelin, isoarthothelin, 4,5-dichlorolichexanthone, and thiophanic acid (K+ yellow, C+ orange, KC+ yellow, and Pd–). Five chemodemes have been discovered in its populations.

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CONTENTS

The structure of xantholepinone A, a new secalonic acid derivative from the lichen *Chrysothrix sulphurella*

John A. Elix
Research School of Chemistry, Building 137,
Australian National University, Canberra, A.C.T. 2601
e-mail: John.Elix@anu.edu.au

Li Liao
Research School of Chemistry, Building 137,
Australian National University, Canberra, A.C.T. 2601
e-mail: li.liao@anu.edu.au

Russell A. Barrow
Plus 3 Australia Pty Ltd, Canberra, Australia
e-mail: plus3australia@gmail.com

Abstract
Xantholepinone A [8,8**'**-dideoxysecalonic acid D] (1) has been isolated from the lichen *Chrysothrix sulphurella* and the structure established by mass spectrometry and NMR spectroscopy. A detailed assignment of the ^{13}C-NMR spectrum of secalonic acid A (2) is also reported.

Introduction
Xantholepinone A was first detected in the lichen *Myelochroa xantholepis* (Mont. & Bosch) Elix & Hale, and subsequently found to be the major component of *Chrysothrix sulphurella* (Räsänen) Kantvilas & Elix (Kantvilas & Elix 2007). It has since been found to be quite widely distributed in other lichen genera, including *Endohyalina* (Elix & Kantvilas 2015, 2016) and *Phaeographis* (Rambold *et al.* 2018). Although xantholepinone A could readily be characterized by thin-layer chromatography (Elix 2014), the structure of this compound remained unknown. This paper describes the structural elucidation of xantholepinone A.

Methods
All nuclear magnetic resonance spectra (NMR) were recorded on a Bruker Biospin GmbH spectrometer at 300 K with probe 5 mm PABBO BB/19F-1H/D Z-GRD Z116098/0258. ^{1}H and ^{13}C NMR experiments were undertaken at 400 MHz and 100 MHz respectively. Low resolution electrospray mass spectra (LRESIMS) were recorded on a Waters Micromass ZMD single quadrupole mass spectrometer using an ionization field of 3500V, source temperature 100°C, desolvation temperature 150°C, coupled to a Waters Alliance 2995 HPLC system. High resolution electrospray mass spectra (HRESIMS) were recorded on a Waters LCT Premier mass spectrometer using an ionization field of 2500 V, source temperature 100°C, desolvation temperature 150°C, coupled to a Waters Alliance 2995 HPLC system. All MS used positive electrospray ionization mode. Fluorescent active thin layer-chromatographic (TLC) plates (silica gel 60 F254) and silica gel (230–400 mesh) for flash chromatography were supplied by Merck Millipore Pty Ltd, Bayswater, Victoria 3153, Australia.

Extraction of *Chrysothrix sulphurella* (Räsänen) Kantvilas & Elix
The lichen *Chrysothrix sulphurella* was collected at Rutherfords Creek Picnic Area, 19 km SE of Nimmitabel, 36°34'29''S, 149°26'36''E, 850 m alt., New South Wales, *J.A. Elix 43053*, 4.ix.2007 (CANB). The dried lichen thallus (3.2 g) was extracted in a Soxhlet extractor with anhydrous diethyl ether (350 mL) for 48 h. The ether extract was concentrated to dryness to yield 113.7 mg of a bright yellow solid. This solid was purified by flash column chromatography over silica gel using 70% ethyl acetate / light petroleum as eluent. Five major bands developed and the slowest moving band was bright yellow. This yellow band was collected from the chromatographic column and concentrated to afford 13.9 mg of a bright yellow solid mixed with a more massive white solid. This white solid had low solubility in organic solvents, so the

mixture was triturated with acetone (5 mL), and the yellow supernatant was concentrated to dryness to afford pure xantholepinone A (1) (1 mg).

The spectroscopic properties of (1) were found to be very similar to those of secalonic acid A (2), secalonic acid E (3) and secalonic acid D (4) (Figure 1), but the chromatographic properties of (1) differed significantly from those of (2), (3) and (4). Unfortunately, no detailed assignment of the ^{13}C-NMR spectrum of secalonic acid A (2) had been reported previously, so we record it here because these assignments were essential in confirming the structure of xantholepinone A (1). Correlations in the gHMBC spectrum of (2) are illustrated in Figure 2.

Structural elucidation of xantholepinone A

Xantholepinone A (1) was obtained as a bright yellow solid with *m/z* $[M+H]^+$ 607.1816 on high resolution ESIMS with a protonated molecule due to $C_{32}H_{31}O_{12}$, thus establishing the molecular formula of this compound as $C_{32}H_{30}O_{12}$. The spectroscopic properties of (1) were very similar to those of secalonic acid A (2), secalonic acid E (3) and secalonic acid D (4) (Figure 1). Assignments in the ^{1}H-NMR spectrum of (1) are summarized in Table 1 together with those of (2), (3) and (4). The ^{1}H-NMR data observed for (2) were identical to that reported previously (El-Elimat *et al.* 2015, 2017). The ^{13}C-NMR spectrum of both (1) and (2) exhibited sixteen carbon signals due to their highly symmetric structures (8/8'-OH ---13.77, s 13.78, s ---13.60, brs (2006) Table 2). In the HSQC spectrum of (1), a carbon signal (δ 18.2) was strongly associated with a doublet proton signal (δ 1.14, 3H), as expected for a methyl bonded to a CH group. The carbon signal (δ 53.1) was associated with a singlet proton signal (δ 3.65, 3H), as expected for a methoxy group in 1. Two singlet proton signals (δ 5.16, 12.53) were not associated with any carbon signals, indicating that these were due to hydroxy groups, the latter (δ 12.53) forming an intramolecular H bond. Two doublet proton signals (δ 6.59, d, J = 8.5 Hz) and (7.53, d, J = 8.5 Hz) were associated with the carbon signals (δ 108.2) and (δ 141.6) respectively, indicating that two adjacent aromatic protons were present in (1). Further the proton signal (δ 7.25, dd, J = 5.6, 2.7 Hz) was associated with a carbon signal (δ 143.6), consistent with the presence of the C6 ethylenic proton. A carbon signal (δ 34.4) was correlated with two proton signals (δ 2.26, 2.74), consistent with the presence of a methylene group on C7. Correlations in the gHMBC spectrum of (1) are illustrated in Figure 4. All these observations were consistent with structure (1) for xantholepinone A, with the same carbon skeleton as secalonic acid A (2) and secalonic acid D (4) but lacking the 8- and 8'-hydroxy groups.

In the NOESY spectrum of (2) (Figure 3), the H11 (δ 1.17) and H5 (δ 3.97) protons are strongly correlated with one another, whereas the H6 (δ 2.47-2.49), H13 (δ 3.65) and 5-OH (δ 5.13) protons are weakly correlated with one-another. These correlations confirm that C11 has β configuration, whereas C12 and 5-OH have α configurations. This was as expected given the established configuration of secalonic acid A (2) (Howard *et al.* 1976).

Similarly in the NOESY spectrum of xantholepinone A (1) (Figure 3), the H11 (δ 1.14) and H5 (δ 3.94) protons were strongly correlated with one another, whereas the H6 (δ 2.39-2.44), H13 (δ 3.65) and 5-OH (δ 5.16) protons were weakly correlated with one another. These correlations suggest that xantholepinone A (1) and secalonic acid A (2) have the same relative stereochemistry at the chiral centres at C5, C6 and C10a, rather than that of (3) in this region. However, the specific rotation of xantholepinone A (1) was determined as $[a]_D^{22}$ = +50 (c 0.1, $CHCl_3$), consistent with that of secalonic acid D (4), the enantiomer of secalonic acid A, with $[\alpha]_D^{25}$ = +61 (c 0.11, CHCl3) (Ren *et al*. 2006). This confirmed that in xantholepinone A. the C11 methyl group has α configuration while the C12 and 5-OH have β configurations. The carbon chemical shifts of compound (1), (2) and (4) were well matched except for C7, C8, C8a and C9, in particular C8 and C8a. As expected, the chemical shift of C8 decreased from δ 179.5 in (2) or δ 178.2 in (4) to δ 143.6 in (1) since C8 is substituted by a hydrogen atom rather than a hydroxy group. At the same time the chemical shift of C8a in (1) increased from δ 102.9 in (2) or δ 101.7 in (4) to δ 131.1.

The structure of xantholepinone A (1) has been elucidated, and shown to be a further representative of a number of secalonic acid derivatives isolated from lichenized fungi (Huneck & Yoshimura 1996).

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Table 1 ^{1}H-NMR data of compounds **1-4** (chemical shifts in δ, coupling constants in Hz)

Position	δ_H mult (*J* in Hz)				
	1 [$(CD_3)_2CO$]	2 [$(CD_3)_2CO$]	2 ($CDCl_3$)*	3 (C_5D_5N)*	4 [$(CD_3)_2SO$] #
3-H	7.53, d (8.5)	7.50, d (8.5)	7.45, d (8.6)	7.42, d (8.6)	7.45, d (8.4)
4-H	6.59, d (8.5)	6.58, d (8.5)	6.63, d (8.6)	6.57, d (8.6)	6.63, d (8.4)
5-H	3.94, dd (11.5, 4.8)	3.97, dd (11.0, 4.6)	3.92, dd (11.2, 0.5)	4.11, d (1.2)	3.81, d (9.5)
6-H	2.39-2.44, m	2.47-2.49, m	2.41, m	2.10, m	2.31, m
7-H	2.26, ddd (20.6, 10.0, 2.7)	2.46, d (13.0)	2.31, dd (19.2, 10.7)	2.40, dd (18.9, 6.3)	2.49, dd (19.8, 6.2)
	2.74, ddd (20.6, 5.6, 5.6)	2.74, d (13.0)	2.73, dd (19.2, 6.4)	2.52, dd (18.9, 11.4)	2.65, dd (19.8, 8.4)
8-H	7.25, dd (5.6, 2.7)	---	---	---	---
11-H	1.14, d (6.6)	1.17, d (6.2)	1.17, d (6.4)	1.17, d (6.9)	1.03, d (6.2)
13-H	3.65, s	3.65, s	3.72, s	3.72, s	3.61, s
1-OH	12.53, s	11.64, s	11.76, s	11.87, s	11.62, s
5-OH	5.16, d (4.8)	5.13, d (4.6)	2.81, d (2.7)	2.60, brs	---
8-OH	---	13.77, s	13.78, s	---	13.60, brs
3'-H	7.53, d (8.5)	7.50, d (8.5)	7.45, d (8.6)	7.42, d (8.6)	7.45, d (8.4)
4'-H	6.59, d (8.5)	6.58, d (8.5)	6.63, d (8.6)	6.57, d (8.6)	6.63, d (8.4)
5'-H	3.94, dd (11.5, 4.8)	3.97, dd (11.0, 4.6)	3.92, dd (11.2, 0.5)	4.11, d (1.2)	3.81, d (9.5)
6'-H	2.39-2.44, m	2.47-2.49, m	2.41, m	2.10, m	2.31, m
7'-H	2.26, ddd (20.6, 10.0, 2.7)	2.46, d (13.0)	2.31, dd (19.2, 10.7)	2.40, dd (18.9, 6.3)	2.49, dd (19.8, 6.2)
	2.74, ddd (20.6, 5.6, 5.6)	2.74, d (13.0)	2.73, dd (19.2, 6.4)	2.52, dd (18.9, 11.4)	2.65, dd (19.8, 8.4)
8'-H	7.25, dd (5.6, 2.7)	---	---	---	---
11'-H	1.14, d (6.6)	1.17, d (6.2)	1.17, d (6.4)	1.17, d (6.9)	1.03, d (6.2)
13'-H	3.65, s	3.65, s	3.72, s	3.72, s	3.61, s
1'-OH	12.53, s	11.64, s	11.76, s	11.87, s	11.62, s
5'-OH	5.16, d (4.8)	5.13, d (4.6)	2.81, d (2.7)	2.60, brs	---
8'-OH	---	13.77, s	13.78, s	---	13.60, brs

* El-Elimat *et al.* (2015)

\# Ren *et al.* (2006)

Table 2 ^{13}C-NMR data of compounds **1, 2** and **4** (chemical shifts in δ)

Position	δ_C		
	1 [$(CD_3)_2CO$]	2 [$(CD_3)_2CO$]	4 [$(CD_3)_2SO$] #
1-C	161.2	160.2	158.9
2-C	118.3	118.6	117.3
3-C	141.6	141.2	140.2
4-C	108.2	108.4	107.5
4a-C	160.8	160.2	158.5
5-C	77.7	77.2	75.2
6-C	31.4	30.8	29.9
7-C	34.4	36.8	35.8
8-C	143.6	179.5	178.2
8a-C	131.1	102.9	101.7
9-C	186.5	188.5	186.6
10-C	108.2	107.5	106.3
10a-C	87.5	86.2	85.2
11-C	18.2	18.3	17.8
12-C	169.9	171.0	170.0
13-C	53.1	53.0	52.6
1'-C	161.2	160.2	158.9
2'-C	118.3	118.6	117.3
3'-C	141.6	141.2	140.2
4'-C	108.2	108.4	107.5
4a'-C	160.8	160.2	158.5
5'-C	77.7	77.2	75.2
6'-C	31.4	30.8	29.9
7'-C	34.4	36.8	35.8
8'-C	143.6	179.5	178.2
8a'-C	131.1	102.9	101.7
9'-C	186.5	188.5	186.6
10'-C	108.2	107.5	106.3
10a'-C	87.5	86.2	85.2
11'-C	18.2	18.3	17.8
12'-C	169.9	171.0	170.0
13'-C	53.1	53.0	52.6

\# Ren *et al.* (2006)

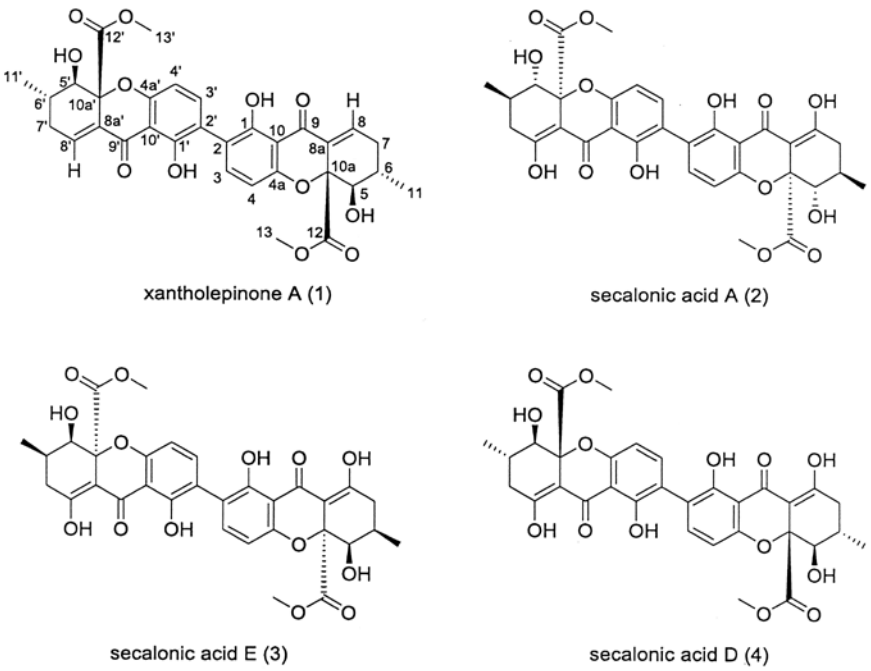

Figure 1. Structures of compounds 1–4

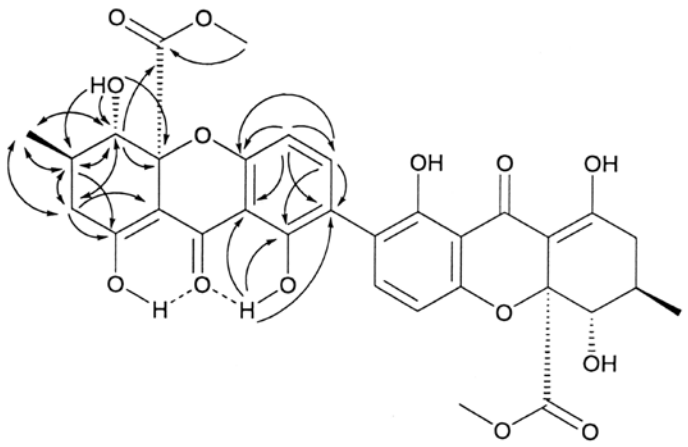

Figure 2. gHMBC correlations of secalonic acid A (2)

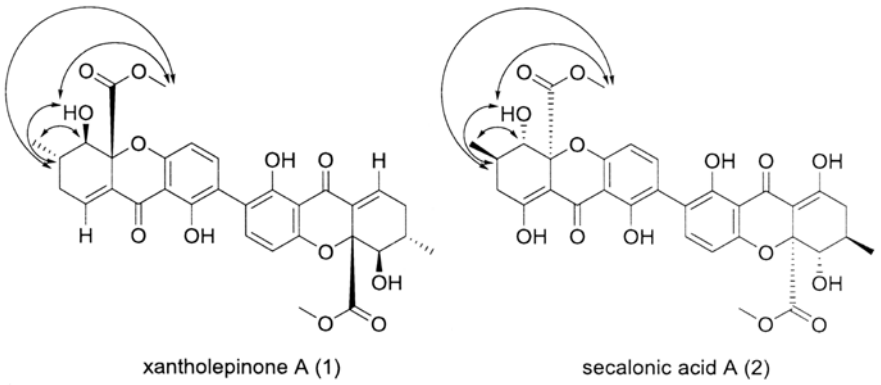

Figure 3. NOESY associations of xantholepinone A (1) and secalonic acid A (2)

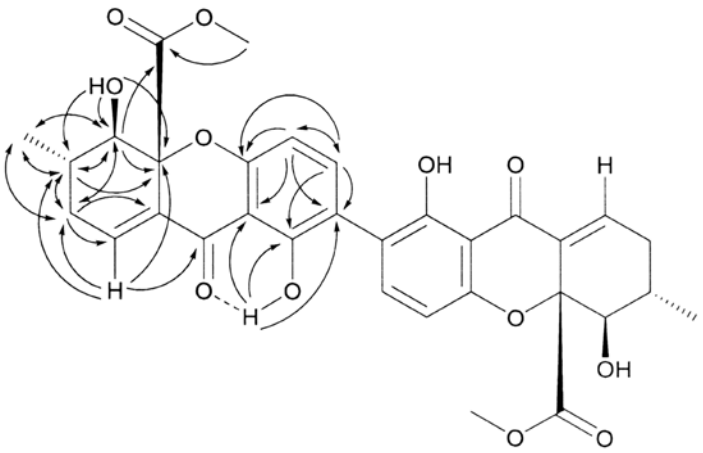

Figure 4. gHMBC correlations of xantholepinone A (1)